AL.2,1986-71 c.2

Coal Report 84-2

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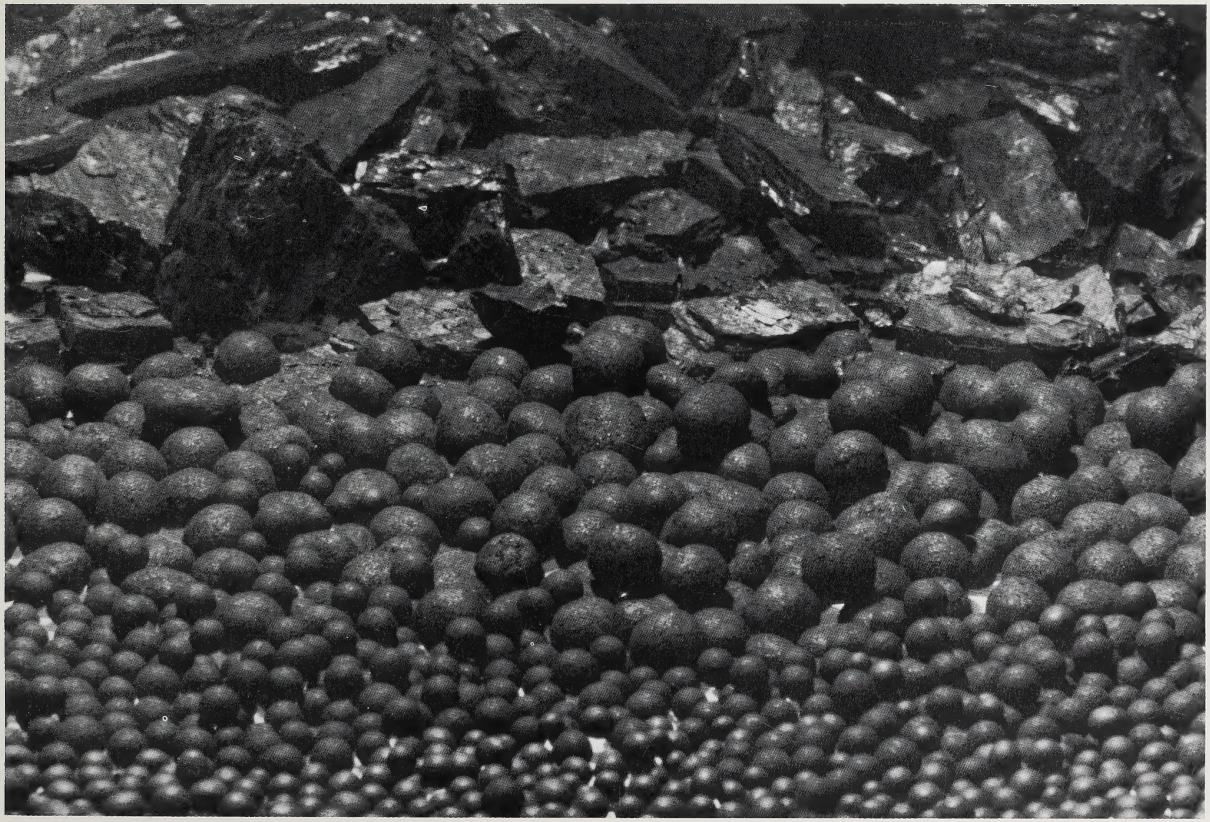
Porosity in Alberta subbituminous coals

S. Parkash, S.K. Chakrabartty and M.P. du Plessis



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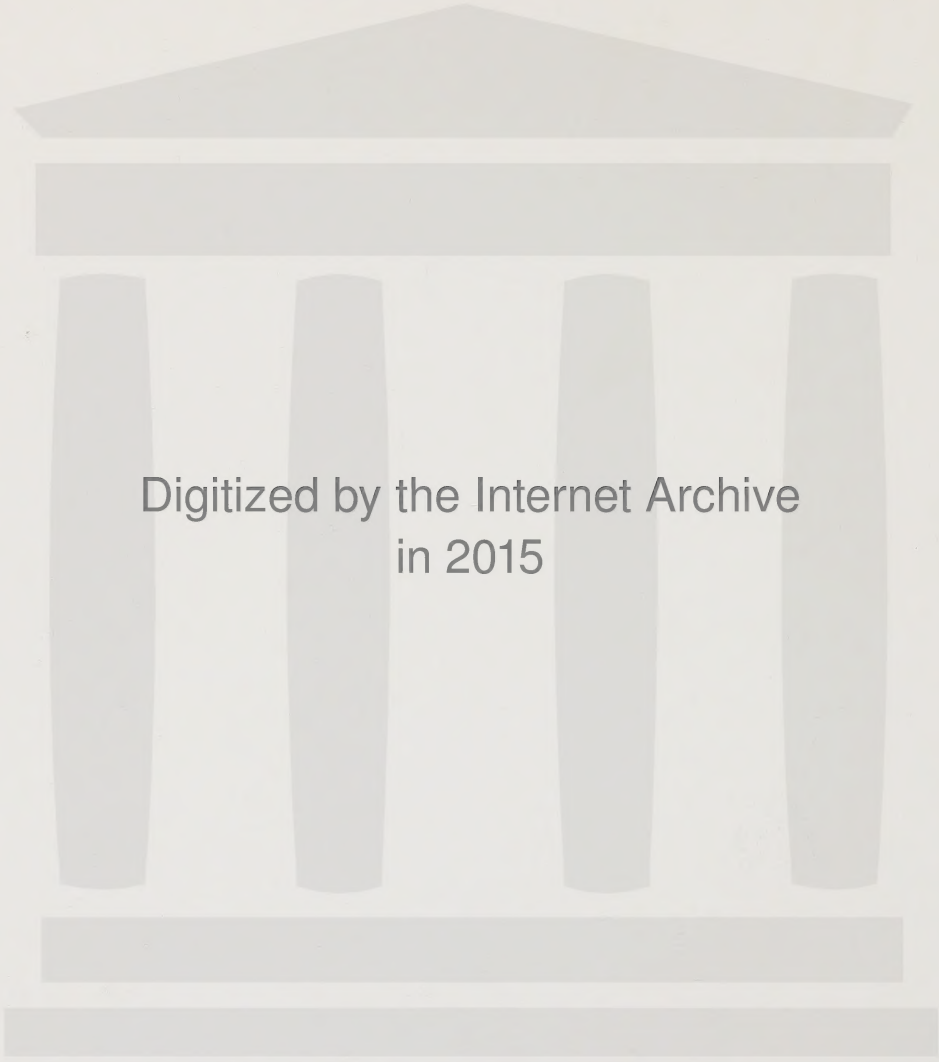
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S. Parkash, S.K. Chakrabartty and M.P. du Plessis

COAL RESEARCH DEPARTMENT, ALBERTA RESEARCH COUNCIL
EDMONTON, ALBERTA, CANADA 1984

Acknowledgments

The authors acknowledge the financial support of both the Alberta Research Council and the Alberta/Canada Energy Resources Research Fund administered by Alberta Energy and Natural Resources.

They are also thankful to K. Lali and M. Holuszko for their assistance in the experimental work to the Editing and Publications Sales Department for producing the report, and to Coal Technology Information Center for information services.

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Abstract

The porosity of coals has a large influence on their behavior during the mining, preparation and utilization of coals. Effective coal utilization requires a much improved understanding, both of the physical description of the pore structure, and of the way in which pore structure influences chemical reactions occurring in coal.

The nature of porosity in 11 Alberta subbituminous coals was studied using different characterization techniques; gas adsorption, helium and mercury displacement, and mercury porosimetry. The coal samples fairly represent the full range of geographic rank and geological variations present in the Alberta Plains coal region. Surface areas calculated from carbon dioxide adsorption at 25°C (varying between 75 and 506 m^2/g) are consistently higher than those calculated from nitrogen at -196°C (varying between 1 and 9 m^2/g). There is no defined influence of the geographic location or rank of the subbituminous coals on their surface areas. The range of the carbon content in the tested coals (73.4 to 76.8 percent) is too narrow to determine the influence of this parameter on surface area and porosity. Nitrogen isotherms at -196°C are of type II or IV, according to the classification of Brunauer and co-workers. Carbon dioxide surface area does not depend on the particle size in the 40 to 550 μm range; the nitrogen surface areas, however, tend to increase with decreasing particle size. Removal of inorganic matter from coals brings about a reduction in surface area.

For subbituminous coals, the methanol densities (varying between 1.522 and 1.696 g/cm^3 (mineral matter free basis) are invariably higher and n-hexane densities (varying between 1.323 and 1.371 g/cm^3) are lower than the corresponding helium densities (1.372 to 1.468 g/cm^3). The mercury density values vary between 1.106 and 1.316 g/cm^3.

Total pore volumes have been measured in the range 1.2 to 3000 nm and then divided into macropores (30 to 3000 nm), transitional pores (2 to 30 nm) and micropores (less than 2 nm). Most of the surface area in coals is located in the micropores. Coals vary widely in their total pore volumes. The porosities range between 9.5 and 22.3 percent. Percent pore volume contained in micropores varies between 29.5 and 75.9, in transition pores between 1.1 and 20.5 and in macropores between 18.5 and 50.0.

In most of the subbituminous coals tested, the pore volume distribution is bimodal, showing two peaks in the diameter range 2 to 5 nm and 7 to 10 nm respectively. The porosity in coals has a large influence on behavior during the mining, preparation and utilization of coals. The reactivity in coal gasification processes depends on the extent of the microporosity in coal. For subbituminous coals, the elevated temperature results in the removal of volatiles in coal, and consequently, creates additional porosity partly due to the enlargement of the pores and partly due to the opening up of previously sealed pores. In direct liquefaction processes, the microporosity in coal enables the donor solvent to come into close contact with, and donate hydrogen to, the free bonds of the molecular fragment.

Introduction

Coal has a unique pore system. The main building blocks of coal are aromatic and hydroaromatic units. It is the poor alignment of these units in three dimensions that produces extensive porosity in coal. X-ray diffraction measurements have distinguished the following three types of structures present in a wide range of coals (Hirsch, 1954):

1. Open Structure is usually found in low rank coals with a carbon content up to about 85 percent. Coals exhibiting this structure are highly porous; the lamellae are connected by cross-links and are randomly oriented in all directions.
2. Liquid Structure is seen in bituminous coals. The lamellae show some orientation and almost no pores are present.
3. Anthracitic Structure is common in higher rank coals with carbon content greater than 91 percent. The orientation of the lamellae increases and cross-links disappear. As a result, high porosity is observed.

The pores in coals vary in size from large cracks to apertures. The empty volume within the pores of a porous material is termed as pore volume. Pores have been classified into three categories by Dubinin (1966):

1. Micropores (diameter less than 1.6 nm);
2. Transitional pores (diameter in the 1.6 to 200 nm range);
3. Macropores (diameter greater than 200 nm).

The surface area of a porous material depends on the pore size distribution — a large pore volume need not always have a large pore surface area.

Coals vary widely in their total pore volumes. The porosities range between 4.1 and 23.2 percent (Gan *et al.*, 1972). In the lower rank coals (carbon content < 75 percent), porosity is primarily due to the presence of micropores. For the quantitative characterization of internal pore structure of coals and chars, one needs to estimate the pore volume, surface area, and pore size distribution.

The significance of the porous texture in coals is summed up very concisely by Mahajan and Walker (1978):

> The porosity in coals has a large influence on behavior during the mining, preparation, and utilization of coals. Unless coals are near outcrops or under lightcover, they contain significant quantities of adsorbed methane in their natural state in the seam. A knowledge of the pore volume and pore size distribution of coals determines the extent and ease of diffusion of methane out of the pore structure during mining. Coal preparation for the market by the removal of mineral matter depends on the specific gravities of the coal and minerals; the specific gravity of the organic phase of coals is partly dependent on porosity. The porosity of coals has its greatest significance in utilization processes. In the liquefaction and gasification conversion processes and in the use of metallurgical coke, chemical reactions occur between gases (or liquids) and coal surfaces, much of which is located in pores. Product molecules must be able to escape rapidly enough from the pores to permit access of fresh reactants. Since the conversion processes involve application of heat, a char is always an intermediate product of the process. Again, the rank of the coal precursor and nature of its pore structure permit a prediction of the type of porosity that will be developed during processing and, hence, an assessment of the

suitability of the coal for a particular conversion process. Furthermore, a number of commercial activated carbons used for gas and water purification are produced by carbonizing coals in the absence of air and, subsequently, activating the char in an oxidizing atmosphere. Knowledge of the porosity of the coal precursor can be helpful in predicting whether a suitable char and, hence, an activated carbon can be produced from the coals.

In the production of carbon molecular sieves from coals for separation of gases (Juntgen, 1977), the quality is controlled by pore size in the starting coals. Coal porosity is detrimental in transporting coal in slurry form with water since (a) water present within the pores does not lead to a more pumpable slurry, and (b) at least 160 to 580 J/g coal of energy would be consumed in subsequent vaporization of water from the coals during their utilization in combustion and gasification processes (Walker, 1981). It is, therefore, apparent that the knowledge of the nature of porosity in coals is a prerequisite in their process utilization.

Pore structure of coal is characterized by such parameters as total pore volume from true density and particle density, pore surface areas from physical adsorption of gases, macropore size distribution from mercury porosimetry, and size distribution of pores below 30 nm from nitrogen isotherms at -196°C (Gan *et al.*, 1972). The experimental approaches used for characterizing pore structure of coals were reviewed recently by Mahajan and Walker (1978) and, therefore, will not be discussed. It is essential, however, to discuss different densities, namely true density, particle density and apparent density, considered for porous materials like coal.

True density

True density of a porous solid is defined as the weight of a unit volume of the pore-free solid. Helium is the smallest atom available and thus has the best chance of penetrating the entire porosity of coals. When determining densities of carbonaceous solids by helium displacement, it has been assumed that the gas is not adsorbed at room temperature. This, however, is not always true (Sharkey and McCartney, 1981; Maggs *et al.*, 1960; Donnet *et al.*, 1968; Kipling *et al.*, 1966). Similarly, the earlier belief (Franklin, 1949) that coal structures have no closed off pores that are inaccessible to helium atoms, is also not always right (Kotlensky and Walker, 1959). Despite these contradictions, it is generally accepted that the helium displacement method to determine true densities for raw coals is the most practical approach since helium adsorption at room temperature is not appreciable enough to cause significant errors in the densities (Maggs *et al.*, 1960).

Particle density

Particle density is the weight of a unit volume of the solid including pores and cracks. It is normally determined from the volume of mercury that the sample displaces under a given pressure.[1] The data of Gan *et al.* (1972) have shown, for the 0.21 to 0.36 mm (7 to 40 mesh) fraction of coal particles, that the interparticle voids have filled with mercury at 413 kPa (60 psi) and that any further mercury penetration at higher pressures would be due to the presence of pores.

Apparent density

Apparent density of a porous solid is normally determined by the pycnometric method in a selected fluid. Apparent density of a porous material depends upon its particle size, range of pore diameters in the solid, molecular dimension of the fluid, its degree of interaction with the solid (that is, swelling and surface effects) and time allowed for penetration of the fluid (Mahajan and Walker, 1978). Densities of coals in organic solvents frequently exceed the helium densities because of absorption (Bond and Spencer, 1957).

Open pore volume and porosity

Total open pore volume (V_T) of the organic phase of coal is calculated from the relationship

$$V_T = \left(\frac{1}{\zeta Hg} - \frac{1}{\zeta He} \right)$$

where ζHg and ζHe are the mercury (particle) and helium (true) densities respectively.

Open pore volume (V) accessible to a given fluid is calculated from

$$V = \left(\frac{1}{\zeta Hg} - \frac{1}{\zeta a} \right)$$

where ζa is the apparent density in the given fluid.

Porosity (P) of a coal is calculated from the relationship

$$P = 100.\zeta Hg \left(\frac{1}{\zeta Hg} - \frac{1}{\zeta He} \right)$$

Surface area

Adsorption of N_2 at -196°C using the Brunauer, Emmett and Teller (BET) equation (1938)

$$\frac{P}{V(Po - P)} = \frac{1}{VmC} + \frac{C - 1}{VmC} \cdot \frac{P}{Po}$$

where V is the volume adsorbed at equilibrium pressure P, Po the saturation vapor pressure of the adsorbate at the adsorption temperature[1], Vm the monolayer capacity and $C = \exp[(E_1 - E_L)/RT]$, where E_1 is the heat of adsorption in the first layer and E_L is the heat of liquefaction of the adsorbate. Thus, C represents the "net" heat of adsorption.

When P/V (Po − P) is plotted against P/Po a straight line should result, with slope $S = (C - 1)/V_mC$ and intercept $i = 1/V_mC$. Solution of the two simultaneous equations gives V_m and C.

[1]To get meaningful mercury densities of coals, it is essential to determine the minimum pressure needed to fill the interparticle void volume.

[1]Po for N_2 at − 196°C is 0.1 MPa.

The specific surface area S (m^2g^{-1}) is related to the monolayer capacity as

$$V = \frac{Vm}{22414} \quad N \cdot A_m \times 10^{-18}$$

where Vm is the monolayer capacity in cm^3 (N.T.P.) per gram of solid, N is Avogadro's number (6.06×10^{23}), A_m is the area in nm^2 (0.162 for N_2) occupied per molecule of adsorbate in the complete monolayer.

Micropores in coals, however, are not completely accessible to N_2 molecules at -196°C due to an activated diffusion process and/or shrinkage of pores (Anderson *et al.*, 1965). Surface areas measured from N_2 adsorption on coals, therefore, are appreciably lower than those expected. According to Anderson *et al.* (1956), N_2 adsorption at -196°C provides a measure of the area contained in pores with diameters greater than about 0.5 nm.

Due to the limitations of the N_2 adsorption method for measuring the surface area of coals, adsorption of CO_2 at 25°C to measure BET surface areas of coals has been suggested (Walker and Kini, 1965). These surface areas greatly exceed those measured from N_2 adsorption for two reasons: (a) CO_2 is a smaller molecule (minimum dimension = 0.33 nm) than an N_2 molecule (minimum dimension = 0.36 nm), and (b) diffusional rates are higher for the smaller CO_2 molecule at the higher adsorption temperature (25°C). Saturation vapor pressure of CO_2 at 25°C (6.4 MPa) is appreciably higher than the atmosphere pressure. The use of the BET equation to calculate surface area, therefore, requires a high pressure adsorption system, which is not very practical.

To calculate surface areas of coals from CO_2 adsorption, Marsh and Siemieniewska (1965) have recommended the use of the Polanyi-Dubinin (P-D) equation:

$$\log V = \log V_o - \frac{0.434BT^2}{\beta^2} \left(\text{Log} \frac{P_o}{p} \right)^2$$

where V is the amount adsorbed at equilibrium pressure P, Vo is the micropore capacity, Po is the saturation vapor pressure of the adsorbate at adsorption temperature T, β is the affinity coefficient of the adsorbate relative to N_2, B is a constant and is a qualitative measure of the average micropore size.

A plot of log V against $(\text{Log Po/p})^2$ gives a straight line with intercept log Vo. The micropore capacity (Vo) multiplied with the cross sectional area of CO_2 molecule (0.253 nm^2) gives the surface area. Almost all the surface area in coals is located in the micropores. Walker and Patel (1970) have shown a good agreement between areas calculated by using the BET equation (high pressure adsorption apparatus) and the P-D equation (by using the vacuum apparatus).

The unique feature of the P-D equation is that it permits the evaluation of micropore volume[1] from CO_2 adsorption data below one atmospheric pressure in a conventional volumetric adsorption apparatus (Walker, 1981).

Coals are associated with different amounts of water which cover, to some extent, the hydrophilic sites in coal (that is, oxygen functional groups and mineral matter); and it therefore blocks entrances of some of the finer micropores. Outgassing of the coal samples overnight at 110°C prior to measuring their surface areas is recommended (Mahajan and Walker, 1978). In spite of the uncertainties associated with the effect of removing moisture from lower rank coals on their porosity, an overnight degassing step at 110°C is the most practical approach.

Time allowed for adsorption can affect surface area values if equilibrium is not reached. Nandi and Walker (1964) have suggested an arbitrary "equilibrium" time of 30 minutes for each sorption point, which has become a fairly common practical approach.

Pore size distribution

Knowledge of surface area and pore volume is inadequate to characterize fully porosity in coals. The distribution of surface area and pore volume in pores of different sizes is another important parameter. To measure such distributions, nitrogen isotherms at -196°C up to relative vapor pressure (P/Po) = 0.93 and mercury porosimetry are frequently used.

Nitrogen isotherms

Nitrogen isotherms on coals are of type II or IV, according to the classification of Brunauer *et al.* (1940). A method developed by Barrett, Joyner and Halenda (1951) (known as the BJH method) for computing the pore volume and size distribution directly from nitrogen isotherm can be successfully applied to adsorbents covering a wide range of pore volume maxima. The pore-volume-distribution curve is obtained by plotting the incremental volume over the incremental diameter ($\triangle V/\triangle d$) against d, the average diameter. Pore radius (r) corresponding to any given point on the isotherm (that is, for any given value of relative pressure P/Po) is calculated from the Kelvin equation:

$$\ln (P/Po) = -(2\, V\, \gamma \cos \theta)/r\, RT$$

where V is the molar volume of the liquid adsorbate, γ the surface tension, θ the contact angle between the liquid and the pore wall (generally assumed to be zero), R the gas constant and T the temperature of the adsorbate (77°K).

There is, however, a controversy regarding the use of the adsorption or desorption branch of the N_2 isotherms for calculating pore size distribution. Cranston and Inkley (1957) have shown good agreement in their analyses from the adsorption and desorption branches for a wide variety of materials. Based on these observations and to save experimental time, Gan *et al.* (1972) have used the adsorption branch of the isotherms to calculate pore size distribution in the diameter range 1.2 to 30 nm.

Mercury porosimetry

Commercial mercury porosimeters capable of operating up to 413 MPa are available. In principal, pore size

[1]Micropore volume V_{CO_2} (in cc/g) = Vo (in mole/g) × 42.7. It is assumed that the molar volume for liquid CO_2 at 25°C is 42.7 cc/mole.

distributions can be determined by forcing mercury into coals at increasing pressures and measuring the volume of mercury penetration as a function of applied pressure P. The diameter d is related to P by the Washburn (1921) equation:

$$d = \frac{-4\gamma\cos\theta}{P} \quad \text{or} \quad d\,(\mu) = \frac{150000}{P(kPa)}$$

where γ is the surface tension of mercury (480 dynes/cm) and θ is the contact angle (140°) between mercury and the pore wall.

Because of the rather high compressibility of coal, a maximum pressure of 69 MPa is commonly used, which corresponds to a pore diameter of 18 nm.

Gan *et al.* (1972) have suggested the following classification to estimate distribution of total pore volume in coals:

a. total open pore volume V_T for pores accessible to helium, as estimated from the helium and mercury densities;
b. pore volume V_1 contained in pores greater than 30 nm in diameter, as estimated from mercury porosimetry;
c. pore volume V_2 contained in pores in the diameter range 1.2 to 30 nm, as estimated from the adsorption branch of the N_2 isotherms;
d. pore volume V_3 contained in pores smaller in diameter than 1.2 nm as estimated from $V_3 = V_T - (V_1 + V_2)$.

Results and discussion

Table 1. Provenance of tested coal samples

Sample no.	Sample site	Geologic formation	ASTM rank
1	Smoky Tower	Paskapoo	Sb A
2	Fox Creek	Paskapoo	Sb B
3	Judy Creek (Swan Hills)	Paskapoo	Sb C
4	Egg Lake (Pickardville)	Horseshoe Canyon	Sb C
5	Highvale	Paskapoo	Sb B
6	Tofield - South	Horseshoe Canyon	Sb C
7	Sissons' - Ardley	Paskapoo	Sb B
8	Vesta (Central Battle River)	Horseshoe Canyon	Sb C
9	Sheerness	Horseshoe Canyon	Sb C
10	Blackfoot - West	Horseshoe Canyon	Sb B
11	Antelope-Bow City (Brooks)	Oldman	Sb B

Provenance of the 11 subbituminous coal samples tested in these investigations is given in table 1. The samples fairly represent the full range of geographic rank and geological variations present in the Alberta Plains coal region (figure 1). Plains coals range in rank (ASTM) from High Volatile C Bituminous to Lignite A, decreasing with distance from the mountains, but by far the largest percentage of mineable reserves are subbituminous B or C. Seams range to 12 feet in thickness and are flat-lying (Campbell, 1983). Figure 1 indicates the three major Plains coal zones: Paskapoo, Horseshoe Canyon and Oldman. The tested samples include three reference coals, subbituminous A (Smoky Tower), subbituminous B (Highvale) and subbituminous C (Vesta-Central Battle River), selected for detailed liquefaction and pyrolysis studies on the basis of accessibility.

Homogenized bulk samples representative of the recoverable coal deposits from the respective regions were obtained by a bucket auger drill rig. Samples were stored in sealed barrels at low temperatures to minimize long-term deterioration. The chemical and petrographic analyses of the coals examined are given in tables 2 and 3 respectively.

A Micromeritics Digisorb (Model 2600), capable of per-

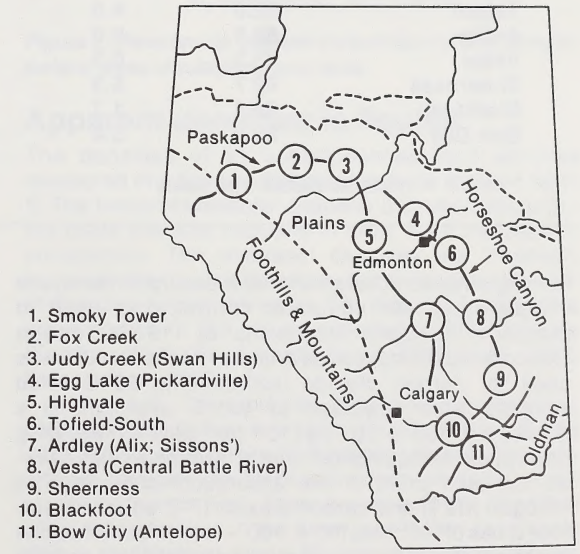

Figure 1. Location of Alberta subbituminous coals tested

Table 2. Elemental composition of Alberta subbituminous coals

Coal identification	ASTM rank	Capacity moisture %	Ash (dry) %	VM (daf) %	Fixed Carbon (daf) %	C % daf	H % daf	N % daf	S % daf	O % (by diff) daf	Calorific value of daf matter kJ/g
Smoky Tower	Sb A	16.0	20.0	43.4	56.6	75.8	5.1	1.7	0.5	16.9	29.8
Fox Creek	Sb B	17.6	17.0	40.0	60.0	75.8	4.2	1.1	0.5	18.4	29.7
Judy Creek	Sb C	nd	16.0	40.5	59.5	75.1	4.1	0.9	0.4	19.5	28.4
Egg Lake	Sb C	25.2	14.6	43.2	56.8	74.2	4.5	1.6	0.4	19.3	28.3
Highvale	Sb B	19.6	10.7	39.6	60.4	75.0	4.4	1.1	0.2	19.3	28.8
Tofield	Sb C	23.3	24.4	43.8	56.2	73.4	4.4	1.6	1.2	19.2	27.9
Ardley	Sb B	19.3	20.0	39.3	60.7	75.7	4.1	1.2	0.5	18.5	29.2
Vesta	Sb C	24.6	12.2	41.9	58.1	74.4	5.0	1.5	0.6	18.5	29.4
Sheerness	Sb C	25.6	10.9	43.2	56.8	73.7	4.6	1.7	0.8	19.2	28.1
Blackfoot	Sb B	16.2	19.4	43.0	57.0	76.8	5.1	1.7	0.8	15.6	28.7
Bow City	Sb B	15.7	13.7	47.1	52.9	75.8	5.4	1.8	0.9	16.1	30.6

daf = dry, ash free

Table 3. Petrographic composition of Alberta subbituminous coals

Coal	Volume % (mmfb)[1] Huminite	Liptinite	Semi-fusinite	Fusinite	Other inertinites	Huminite reflectance (random) %
Smoky Tower	70.0	6.4	8.6	4.3	10.7	0.49
Fox Creek	82.6	1.5	9.5	4.5	1.9	0.40
Judy Creek	72.4	5.3	8.1	9.1	5.1	0.38
Egg Lake	92.4	4.2	0.8	0.4	2.2	0.33
Highvale	74.6	2.1	22.2	1.1	-	0.43
Tofield	92.0	4.0	2.0	1.0	1.0	0.39
Ardley	59.5	9.0	18.9	7.5	5.1	0.45
Vesta	73.3	0.3	8.9	3.3	14.1	0.40
Sheerness	92.7	5.3	1.2	0.8	-	0.42
Blackfoot	91.4	1.7	1.7	1.3	3.9	0.43
Bow City	82.9	3.4	3.7	3.4	6.6	0.46

[1] mmfb = mineral matter free basis

forming physical adsorption and/or desorption analyses completely under computer control, was used to measure nitrogen isotherms at -196°C and a Micromeritics Surface Area Analyser (Model 2100D) was used for carbon dioxide isotherms at 25°C. Coal samples were degassed at 100°C overnight at a pressure of 133 × 10^{-5} pa (10^{-5} torr) before measuring adsorption. An equilibrium time of 30 minutes was allowed for each point of the adsorption isotherm. The nitrogen (BET) and carbon dioxide (P-D equation) surface areas of the coals (60 × 100 – mesh fractions) on a dry-mineral-matter-containing basis (mmcb) are given in table 4.

Surface areas calculated from carbon dioxide adsorption at 25°C are consistently higher than those calculated from nitrogen at -196°C. The low N_2 areas of coals measured at -196°C are due to very low diffusion rates of N_2 (Mahajan and Walker, 1978).

According to Gan *et al.* (1972), finely divided mineral particles distributed in the coal organic matrix[1] are not accessible to N_2 at -196°C, and the reported carbon dioxide areas would not be too much affected by the surface

[1]Nitrogen surface area of the mineral matter obtained from the low temperature ashing of coals could be as high as 10 m^2/g (S. Parkash, unpublished data).

Table 4. Surface area of Alberta subbituminous coals

Coal	ASTM rank	Surface area m²/g (mmcb)	
		Nitrogen[1]	CO_2[2]
Smoky Tower	Sb A	7.0	234
Fox Creek	Sb B	6.4	239
Judy Creek	Sb B	9.3	149
Egg Lake	Sb C	4.9	292
Highvale	Sb B	3.2	205
Tofield	Sb C	7.4	299
Ardley	Sb B	8.5	75
Vesta	Sb C	2.8	286
Sheerness	Sb C	2.9	314
Blackfoot	Sb B	2.8	506
Bow City	Sb B	1.1	268

[1]BET method
[2]Polanyi-Dubinin method
mmcb = mineral matter containing basis

area contributed by mineral matter, since the total area, for all coal samples, is usually more than 100 m²/g.

As rightly pointed out by Sharkey and McCartney (1981), there has been extensive deliberation on the validity and justification of reporting the surface areas of microporous adsorbents. To evaluate surface area, it is not possible to assign a definite value to the cross-sectional area of the adsorbate molecules. Dubinin (1960) argues that because there is an adsorption force field in the entire volume of micropores, adsorption results in volume filling of the micropores. Because of this, Dubinin emphasizes that the concept of layer-by-layer filling (as is envisaged in the derivation of the BET equation) and of area of micropores is meaningless. Surface area of coals has no physical significance and reporting monolayer volumes or total volumes of sorbate uptake is far more logical (Spencer and Bond, 1966).

There is no consistent influence of the geographic location or rank of the subbituminous coals on their surface areas estimated either from nitrogen or carbon dioxide adsorption isotherms. The nitrogen surface area varies in the range 1 to 9 m²/g and the CO_2 surface area varies in the range 75 to 506 m²/g. The gel-like structure in some low rank subbituminous coals may be irreversibly altered upon drying and thus, low N_2 areas may be apparent. The relationship between CO_2 and N_2 surface area is shown in figure 2.

The range in carbon content of the tested coals is very narrow (73.4 to 76.8 percent) and, therefore, inappropriate to determine its influence on the surface area. A plot of surface areas versus carbon content is shown in figure 3.

Typical adsorption isotherm of nitrogen at -196°C on a coal is shown in figure 4. Based on BET classification (Brunauer *et al.*, 1940), figure 4 shows a type II isotherm. P-D plots for CO_2 adsorption at 25°C are shown in figure 5.

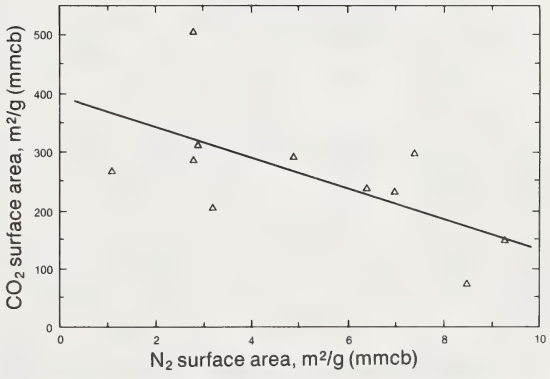

Figure 2. Relationship between carbon dioxide and nitrogen surface areas of subbituminous coals

Apparent densities in liquids

The densities of 11 subbituminous coal samples measured in n-hexane and methanol are listed in table 5. The helium (molecular diameter 0.2 nm) densities of the coals are also included in table 5 for the sake of comparison. The methanol densities are invariably higher and n-hexane densities are lower than the corresponding helium densities. The data are in complete agreement with the values reported in the literature (Franklin, 1949; Bond and Spencer, 1957; Toda, 1972; Nelson *et al.*, 1980).

In figure 6, the densities measured in n-hexane, methanol and helium are plotted against dry-ash-free carbon contents (73.4 to 76.8 percent range) of 11 subbituminous coals. All the densities increase fairly linearly with carbon content. There are reports that densities show higher values in the lower and higher rank coals with a minimum at about 87 percent carbon content (Toda, 1972).

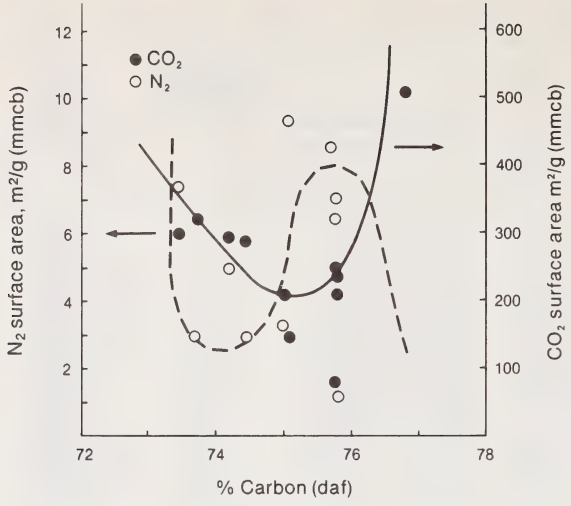

Figure 3. Variation of nitrogen and carbon dioxide surface areas of subbituminous coals with carbon content

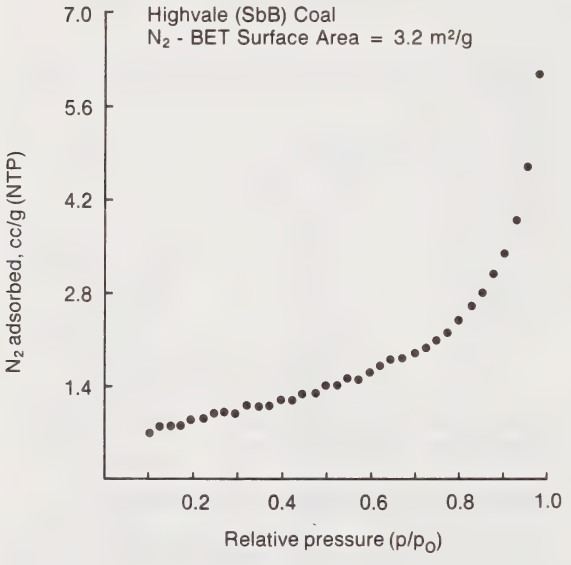

Figure 4. A typical adsorption isotherm of nitrogen at -196°C on a subbituminous coal

The lower n-hexane densities are due to the much larger size of an n-hexane molecule (0.5 nm) compared to that of a helium molecule (0.2 nm). However, the difference between methanol densities and helium densities cannot be explained by the difference in size between methanol (0.4 nm) and helium molecules (0.2 nm). The excess of the density in methanol is attributed to the contraction of methanol on the coal surface (Franklin, 1948).

Coals invariably contain different amounts and types of mineral matter that usually have high densities. The densities, usually, are corrected for the mineral matter by the equation

$$X/\zeta_m + (1 - X)/\zeta_c = 1/\zeta$$

where ζ_m is the density of mineral matter, ζ_c the corrected density of the organic phase of coal, ζ the original uncorrected density, and X the fractional mineral matter content by weight. The density of the mineral matter present in coals has been reported to differ little from that of the ash itself (Tschamler and de Ruiter, 1963). When the ash density is not determined experimentally, average ash densities of 2.7 g/cm³ are recommended (van Krevelen, 1961). In these investigations, ash densities for tested subbituminous coals, determined experimentally, average to 2.33 g/cm³. This value has been used for making necessary corrections for mineral matter. Densities corrected for mineral matter are included in table 5.

The contraction ratios of methanol in the pores of coal (entrance diameter less than 0.5 nm) are calculated from the relationship[1]

$$(V_{n\text{-Hex}} - V_{CH_3OH})/(V_{n\text{-Hex}} - V_{He})$$

as proposed by Toda (1972). The contraction ratios in the subbituminous coals are two to three, except for two coals (table 6). This would mean that the methanol in the pores of low rank coals is contracted to one half to one third of the volume in the normal liquid state. According to Dubinin (1960) the contraction effect of methanol in the pores of coal cannot be so large at the temperature, 25°C, at which the density is measured. It is difficult to explain such a large volume change of methanol, even if some chemical reaction occurs on the surface of coal. It is more logical to assume that:

a. the helium molecule is denied access to part of the smaller pores by the activated diffusion effect, and/or
b. the methanol molecule can penetrate into the closed pores as a result of an imbibition (absorption) effect.

Mercury and helium densities

The mercury density values of 11 coals, calculated from measurement of mercury displaced by the coal samples at 410 kPa, are given in table 7. The variation of mercury density (dry-ash-free basis) with carbon content (dry-ash-free) is shown in figure 7. A regular decrease appears in mercury density with an increase in carbon content (73.4 to 76.8 percent range). Toda (1972) and Gan *et al.* (1972) also observed the same trend for Japanese and American coals with 70 to 80 percent (daf) carbon content.

The densities of all the 11 subbituminous coals, determined by helium displacement at 25°C, are included in table 7. A plot of variation of helium density with carbon content indicates a maximum for samples with dry-ash-free carbon content approaching 75 percent. On both sides of this carbon content (< or > 75 percent) there is a general decrease in density (figure 8). Gan *et al.* (1972) have shown a decrease in helium density with increase in carbon content in the 71 to 80 percent range for American coals.

[1] $V_{n\text{-hex}}$, V_{CH_3OH} and V_{He} are the specific volumes in n-hexane, methanol and helium respectively.

Total open-pore volumes, calculated from the differences of reciprocals of mercury and helium densities (table 7), are shown in table 8. Percentages of the open porosity of the coals, calculated from densities, are also included in table 8. The variation of total open-pore volume (dry-ash-free basis) with carbon content (dry-ash-free) is shown in figure 9. A sort of linear correlation can be imagined between porosity and carbon content of these subbituminous coals (figure 10). This, of course, should not be generalized strictly.

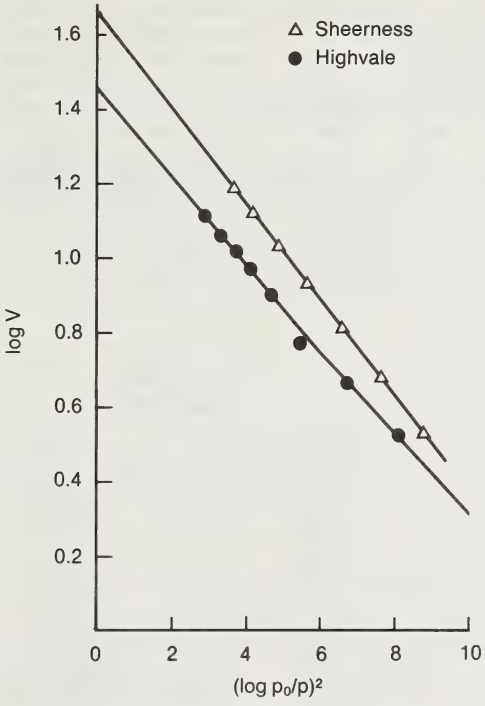

Figure 5. Polanyi-Dubinin plots for CO_2 adsorption on coals at 25°C

Pore size distribution

Pore size distributions, in the diameter range 1.2 to 30 nm, of 11 subbituminous coals were calculated from the adsorption branch of the nitrogen isotherms at -196°C, using the method of Barrett *et al.* (1951). The data, as a sample, are given in table 9 for only one coal.

The pore volume distribution curve was obtained by plotting the incremental volume over the incremental diameter ($\triangle v/\triangle d$) against d, the average diameter. A

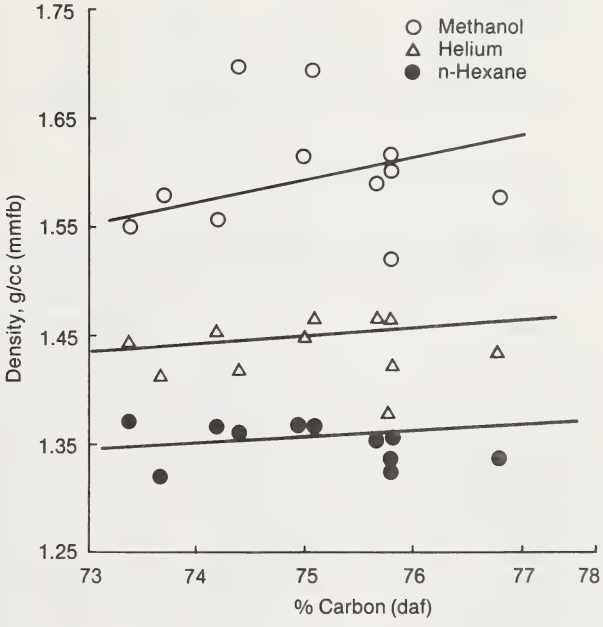

Figure 6. Variation of density of subbituminous coals with carbon content

Table 5. Densities of Alberta subbituminous coals at 25°C

Coal	Density, g/cc (mmcb) measured with:			Density, g/cc (mmfb) measured with:		
	n-Hexane	Methanol	Helium	n-Hexane	Methanol	Helium
Smoky Tower	1.483	1.720	1.545	1.360	1.616	1.426
Fox Creek	1.422	1.683	1.555	1.327	1.606	1.467
Judy Creek	1.465	1.774	1.561	1.367	1.696	1.468
Egg Lake	1.455	1.642	1.537	1.368	1.563	1.452
Highvale	1.432	1.673	1.511	1.369	1.617	1.449
Tofield	1.524	1.683	1.592	1.371	1.551	1.445
Ardley	1.480	1.701	1.583	1.355	1.593	1.465
Vesta	1.431	1.754	1.487	1.358	1.696	1.417
Sheerness	1.388	1.636	1.470	1.323	1.579	1.407
Blackfoot	1.454	1.687	1.550	1.333	1.581	1.435
Bow City	1.413	1.598	1.453	1.329	1.522	1.372

mmcb = mineral matter containing basis
mmfb = mineral matter free basis

Table 6. Contraction ratios of methanol in pores of Alberta subbituminous coals

Coal	$(V_{n\text{-}Hex} - V_{CH_3OH})/(V_{n\text{-}Hex} - V_{He})$
Smoky Tower	3.4
Fox Creek	1.8
Judy Creek	2.8
Egg Lake	2.2
Highvale	2.8
Tofield	2.3
Ardley	2.0
Vesta	4.9
Sheerness	2.7
Blackfoot	2.2
Bow City	4.1

V is specific volume = 1/density

typical distribution curve for Highvale (subbituminous B) coal is shown in figure 11. In most subbituminous coals, the pore volume distribution is bimodal, showing two distinct peaks in the diameter range 2 to 5 nm and 7 to 10 nm respectively.

The cumulative pore volumes, contained in pores greater than 30 nm in diameter, were measured by mercury porosimeter. The data are given in table 10, column 3. Figure 12 shows a typical result of the volume of mercury penetration against the absolute pressure applied (or pore diameter) for Highvale subbituminous B coal. Percent pore volume distribution in the pore diameter range 18 to 3000 nm is shown in figure 13.

Gross pore volume distribution in the indicated pore diameter range for the 11 subbituminous coals are given in table 10, following the classification of Gan *et al.* (1972). In Smoky Tower (Sb A), Sheerness (Sb C), Blackfoot (Sb B) and Bow City (Sb B) samples, more than 70 percent of the pore volume (V_T) is contributed by pores of diameter less than 1.2 nm (V_3), while in the remaining coals (except Fox Creek Sb B) the micropore

Table 7. Particle and true densities of Alberta subbituminous coals

Coal	Particle density (ζ_{Hg}) g/cc		True density (ζ_{He}) g/cc	
	mmcb	mmfb	mmcb	mmfb
Smoky Tower	1.284	1.154	1.545	1.426
Fox Creek	1.412	1.316	1.555	1.467
Judy Creek	1.262	1.161	1.561	1.468
Egg Lake	1.382	1.291	1.537	1.452
Highvale	1.375	1.311	1.511	1.449
Tofield	1.416	1.257	1.592	1.445
Ardley	1.324	1.195	1.583	1.465
Vesta	1.316	1.241	1.487	1.417
Sheerness	1.212	1.145	1.470	1.407
Blackfoot	1.241	1.115	1.550	1.435
Bow City	1.192	1.106	1.453	1.372

Table 8. Total pore volume and porosity of Alberta subbituminous coals

Coal $2c^3/g$ (mmfb)	Total pore volume, (mmfb)	% Porosity
Smoky Tower	0.166	19.1
Fox Creek	0.078	10.3
Judy Creek	0.180	20.9
Egg Lake	0.105	13.6
Highvale	0.073	9.5
Tofield	0.104	13.0
Ardley	0.154	18.4
Vesta	0.100	12.4
Sheerness	0.162	18.6
Blackfoot	0.200	22.3
Bow City	0.175	19.4

Total Pore Volume $V_T = \left(\frac{1}{\zeta Hg} - \frac{1}{\zeta He} \right)$ % Porosity = $100\,(1 - \zeta Hg/\zeta He)$

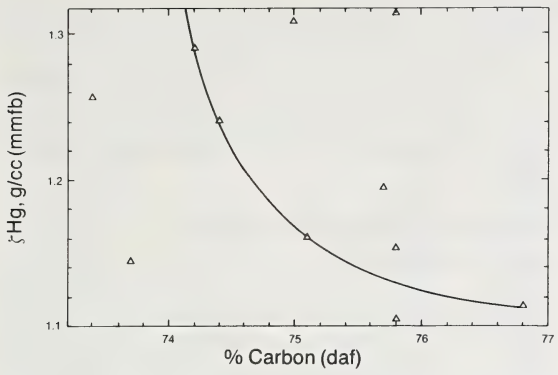

Figure 7. Variation of particle density (ζHg) of subbituminous coals with carbon content

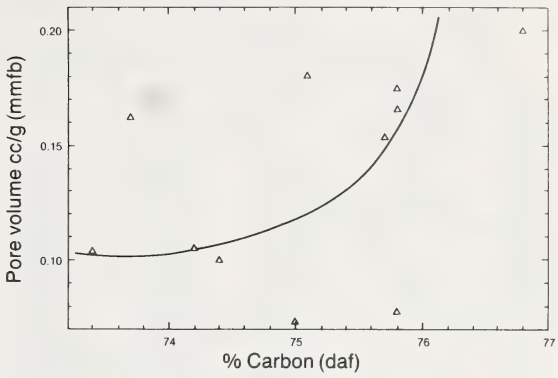

Figure 9. Variation of total pore volume of subbituminous coals with carbon content

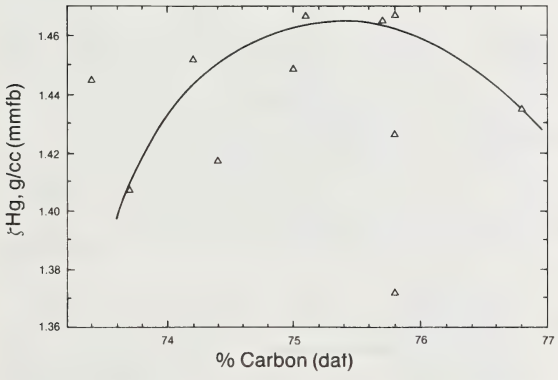

Figure 8. Variation of true density (ζHe) of subbituminous coals with carbon content

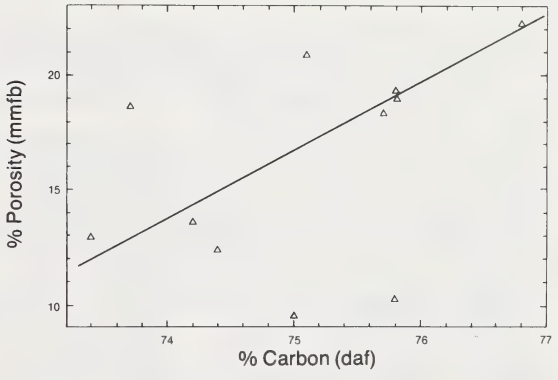

Figure 10. Variation of porosity of subbituminous coals with carbon content

Table 9. Adsorption pore volume and pore area — Highvale coal

Pore diameter range, nm	Average diameter, nm	Pore volume (cc/g)	Cumulative pore volume	Pore area (m^2/g)	Cumulative pore area
61.25 - 52.81	56.24	0.000693	0.000693	0.049	0.049
52.81 - 39.02	43.70	0.001020	0.001713	0.093	0.142
39.02 - 33.38	35.60	0.000622	0.002334	0.070	0.212
33.38 - 25.32	28.11	0.000780	0.003114	0.111	0.323
25.32 - 21.52	22.88	0.000632	0.003746	0.110	0.433
21.52 - 16.78	18.44	0.000568	0.004315	0.123	0.557
16.78 - 13.76	14.85	0.000660	0.004975	0.178	0.735
13.76 - 10.81	11.83	0.000633	0.005608	0.214	0.949
10.81 - 8.78	9.49	0.000453	0.006061	0.191	1.140
8.78 - 6.98	7.59	0.000407	0.006468	0.214	1.354
6.98 - 5.59	6.05	0.000516	0.006984	0.341	1.695
5.59 - 4.49	4.84	0.000379	0.007363	0.313	2.008
4.49 - 3.58	3.86	0.000345	0.007707	0.357	2.365
3.58 - 2.85	3.07	0.000339	0.008047	0.442	2.808
2.85 - 2.12	2.30	0.000328	0.008375	0.570	3.377

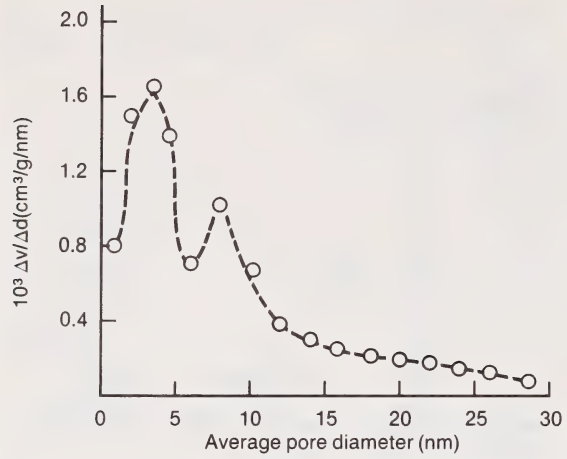

Figure 11. Pore volume distribution in Highvale coal from nitrogen adsorption isotherm

volume (V_3) accounts for 50 to 70 percent of the total pore volume. Smaller pores are primarily responsible for contributing surface area. Some anomalies to this fact, observed in these data, are not unusual (Gan *et al.* 1972) and are difficult to explain.

Pore volumes in the coals contained in pores varying in size from 30 nm in diameter to the smallest pores accessible to helium at 25°C, are calculated by subtracting V_1 (measured by mercury intrusion) from V_T, the total open pore volume (table 11). The data indicate that for some coals $^{V}CO_2$, calculated micropore volume from CO_2 adsorption data, exceeds ($V_T - V_1$) that represents the volume contained in pores varying in size from 30 nm in diameter to the smallest pores accessible to helium. The larger $^{V}CO_2$ values compared to ($V_T - V_1$) values may be due to the ability of CO_2 to induce swelling in coals (Toda, 1972; Briggs and Sinha, 1933). This, of course, may not be the reason, especially when it seems highly unlikely that CO_2 could be imbibed in the coal to such an extent to account for the observed difference between $^{V}CO_2$ and ($V_T - V_1$).

Effect of particle size on surface area

It is usually argued that since adsorption of gases on microporous coals is often diffusion-controlled, rates of adsorption can generally be enhanced by decreasing the particle size. Results given in table 12 show the CO_2 surface area does not depend very much on the particle size in the range of 40 to 550 μm. For nitrogen, however, the equilibrium is not attained for a long time and, hence, surface area tends to increase with decreasing particle size.

Effect of inorganic matter on surface area

Coals are associated with discrete mineral matter and trace elements. Inorganic matter present in coals usually has a catalytic effect on gasification and liquefaction behavior. To understand the contribution of mineral matter on coal porosity, coals were demineralized by acid treatment with HCl and HF. Results given in table 13 for five coals show that removal of inorganic matter from coals brings about, invariably, some reduction in surface area. The changes in surface area upon acid treatment were attributed by Mahajan and Walker (1979) to: (i) physical removal of inorganic matter from the aperature-cavity type porosity, (ii) bonding of HCl/HF to basic nitrogen present in coal structure, and (iii) adsorption of HCl/HF. The removal of inorganic matter from coal by acid treatment is quite a drastic procedure, which may alter the basic coal structure and thus, proper caution should be exercised to interpret the data for demineralized coal samples.

The concept of surface area has been criticized for two reasons:

1. It is difficult to assign a perfectly correct value for the cross sectional area of an adsorbed molecule. In slit-shaped pores present in coals (Walker *et al.*, 1966), a molecular area from two to three times that found on a flat surface is perhaps more reasonable.
2. Dubinin (1966) has advocated that the adsorption force field in the entire volume of the micropores results in volume filling of the pores instead of layer-by-layer filling, which is the basis on which the BET equation was derived.

There is merit in Spencer and Bond's (1966) suggestion that surface area of coals should not be reported; instead their monolayer volumes or total volumes of sorbate uptake should be reported.

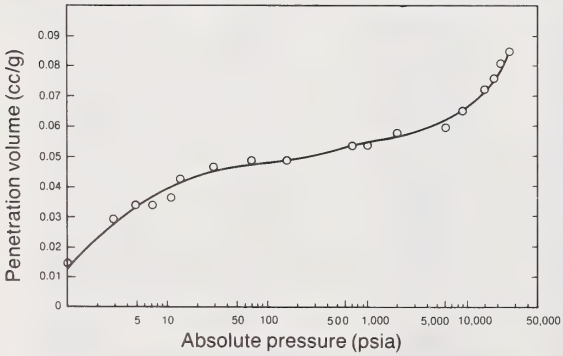

Figure 12. Porosimeter data plot for Highvale (Sb B) coal

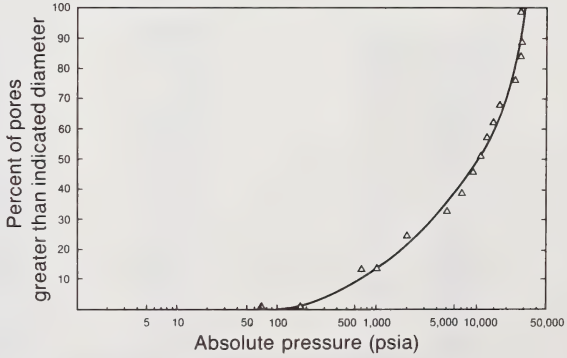

Figure 13. Percent pore distribution in Highvale (Sb B) coal

Table 10. Gross pore volume distribution in Alberta subbituminous coals

Coal	Pore volume, cc/g (mmfb)				% Pore volume (mmfb)		
	V_T	V_1	V_2	V_3	V_1	V_2	V_3
Smoky Tower	0.166	0.035	0.013	0.118	21.1	7.8	71.1
Fox Creek	0.078	0.039	0.016	0.023	50.0	20.5	29.5
Judy Creek	0.180	0.043	0.023	0.114	23.9	12.8	63.3
Egg Lake	0.105	0.028	0.009	0.068	26.7	8.5	64.8
Highvale	0.073	0.021	0.009	0.043	28.8	12.3	58.9
Tofield	0.104	0.036	0.016	0.052	34.6	15.4	50.0
Ardley	0.154	0.050	0.021	0.083	32.5	13.6	53.9
Vesta	0.100	0.034	0.009	0.057	34.0	9.0	57.0
Sheerness	0.162	0.031	0.008	0.123	19.1	4.9	75.9
Blackfoot	0.200	0.037	0.006	0.157	18.5	3.0	78.5
Bow City	0.175	0.043	0.002	0.130	24.6	1.1	74.3

V_T = Total open pore volume, for pores accessible to helium at room temperature, calculated from the relationship

$$V_T = \left(\frac{1}{\rho Hg} - \frac{1}{\rho He} \right)$$

V_1 = Pore volume contained in pores 30 nm in diameter, calculated from porosimetry.

V_2 = Pore volume contained in pores in the diameter range 30 to 2 nm, calculated from N_2 isotherms.

V_3 = Pore volume contained in pores 2 nm in diameter, being equal to $V_T - (V_1 + V_2)$.

Table 11. Comparison of micropore volume estimated from CO_2 adsorption on Alberta subbituminous coals with $(V_T - V_1)$

Coal	V_{CO_2}, cc/g (mmfb)	$(V_T - V_1)$, cc/g (mmfb)
Smoky Tower	0.083	0.131
Fox Creek	0.081	0.039
Judy Creek	0.050	0.137
Egg Lake	0.096	0.077
Highvale	0.066	0.052
Tofield	0.176	0.068
Ardley	0.025	0.104
Vesta	0.091	0.066
Sheerness	0.099	0.131
Blackfoot	0.176	0.163
Bow City	0.087	0.132

Table 12. Effect of particle size on surface area and pore volume — Vesta coal

Mesh size	% Ash (dry)	Surface area m^2/g (mmcb)		Pore Volume, cc/g (mmcb)	
		N_2	CO_2	N_2 isotherm (2-52 nm diameter range)	CO_2 isotherm (<2 nm diameter)
− 40 + 65	8.2	3.0	237	0.0056	0.067
− 65 + 100	13.5	2.5	249	0.0052	0.069
− 100 + 150	14.6	2.8	252	0.0057	0.070
− 150 + 200	13.1	2.8	261	0.0063	0.073
− 200 + 325	16.9	3.8	232	0.0074	0.065

Table 13. Effect of inorganic matter removal on surface area of Alberta subbituminous coals

Coal	Inorganic matter, % (dry)		N_2-BET surface area, m^2/g (mmcb)		Pore volume, cc/g (mmcb)	
	Raw coal	Acid-treated coal	Raw coal	Acid-treated coal	Raw coal	Acid-treated coal
Smoky Tower	20.0	2.5	7.0	2.1	0.010	0.005
Highvale	10.7	1.2	3.2	1.9	0.008	0.004
Vesta	12.2	1.8	2.8	2.7	0.008	0.007
Fox Creek[1]	34.9	15.0	12.7	6.4	0.024	0.013
Judy Creek[1]	45.4	16.0	31.1	9.3	0.051	0.019

[1]Water-washed to remove inorganic matter

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